Evaluation of damage depth on arginine films with molecular depth profiling by Ar cluster ion beam

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Ion-induced damage on organic materials has been evaluated with secondary ion mass spectrometry (SIMS). However, conventional sputter beams, such as SF_5^+ , C_{60}^+ cannot etch the organic materials without inducing damage, and it is difficult to evaluate the depth distribution of the damage in these materials. Large gas cluster ion can etch organic materials without damage, and in this study the damaged layer thickness was evaluated by molecular depth profiling with Ar cluster ion beam. Arginine films were irradiated with 10 keV Ga^+ at a dose of 1.0×10^{14} ions/cm² with the aim of forming a damaged layer on the surface. The chemical structure of arginine was seriously damaged, as indicated by the non-detection of protonated arginine molecular ions after Ga^+ ions irradiation. The peak intensity of the protonated arginine ion increased with increasing sputtering depth and saturated at the depth of about 30 nm. This value agreed with the projection range of the Ga^+ ion indicating that the depth of the ion-induced damage was the same as projection range of the ion. Ion-induced damage layer thickness on arginine films were accurately evaluated by molecular depth profiling with Ar cluster ion beam.

Key words: ToF-SIMS, molecular depth profiling, Ar cluster, arginine

1. INTRODUCTION

Ion beam have been used lately as processing and analytical tools for organic materials in various fields. However, ion beams damage the chemical structure of the organic materials. Until now, the ion-induced damage has been evaluated by secondary ion mass spectrometry (SIMS) [1–3], a surface analysis technique that uses mass spectrometry in conjunction with secondary ions emitted from the materials surface. The SIMS method is surface sensitive because the escape depth of the secondary ion is about 1 nm [4]. To investigate the bulk of various materials, the technique called “depth profiling”, which combines analysis and sputtering, is used. In recent works, a dual beam technique has been used for depth profiling, with small cluster ions such as SF_5^+ , C_{60}^+ or low-energy O_2^+ as the sputtering beam and Ga^+ , Bi_n^+ , or Au_n^+ ($n \leq 3$) as the analysis beam [2,3,5]. However, there are some severe problems in depth profiling of organic materials with conventional sputter beam, because of ion-induced damage accumulation effects, and these problems prevent accurate evaluation of the ion-induced damage layer thickness.

A large gas cluster is an aggregate that consists of hundreds of atoms or molecules of a gaseous substance. Because of the large mass-to-charge ratio, the energy per atom or molecule of cluster ion beams is very low and low-energy irradiation can be realized. Large gas cluster ion beam processing exhibits unique characteristics for inorganic materials, such as high-rate sputtering [6], surface smoothing [7,8] and shallow implantation [9,10]. In addition, large gas cluster ion beams can also etch organic materials with high sputtering yield [11] and

without damage [12,13], and molecular depth profiling was demonstrated for polymer materials, for which depth profiling with the conventional sputter beam does not work [11]. Moreover, in depth profiling with Ar cluster the depth resolution was higher than with conventional sputter beams [3,14]. Thus, it was expected that depth profiling with Ar cluster beams would enable a more accurate evaluation of the damage layer thickness. In this study, the thickness of the ion-induced damaged layer was evaluated by molecular depth profiling with Ar cluster ion beam.

2. EXPERIMENTAL

In a previous work [15], Ar cluster ion was used as the analytical beam and the protonated arginine molecular ion was detected with high intensity. Thus, arginine (mass number 174) was chosen as a typical organic sample in this work. Arginine thin films were prepared by spin-coating onto a Si wafer at 4000 rpm for 30 s. The wafers were sonicated in deionized water and acetone, prior to the coating. Figure 1 presents a schematic diagram of the atomic ion irradiation setup. Arginine samples were irradiated with 10 keV Ga^+ ions at an incidence angle of 35° with respect to the surface normal. The total ion fluence on the sample was 1×10^{14} ions/cm², which was higher than the static SIMS limit of atomic ions (about 1.0×10^{13} ions/cm²) [16–18]. The maximum projection range of 10 keV Ga^+ ion into arginine as calculated by the TRIM simulation (SRIM 2008) was about 30 nm. The sputtering depth for arginine samples with 10 keV Ga^+ ions at the dose of 1×10^{14} ions/cm² was about 3 nm.

The TRIFT III system (ULVAC phi, Kanagawa,

Figure 1. Schematic diagram of the atomic ion irradiation setup of the arginine film. The film was irradiated with 10 keV Ga^+ at a dose of 1×10^{14} ions/ cm^2 at an incidence angle of 35° with respect to the surface normal.

Japan) was equipped with an Ar cluster ion source. The large Ar cluster ions were produced by a gas cluster ion beam (GCIB) apparatus. The GCIB technique and equipment are described in detail in refs [19,20], and the source for SIMS is described in ref. [11]. In this study, a scanning deflector was used as second chopper to chop the primary cluster ion beams for SIMS analysis. The incident energy of the primary Ar cluster ion beams was 10 keV, the current was 10–16 nA and the beam diameter was about 300 μm . The mean cluster size used in this study was 3000 atoms. The constituent atom of the Ar cluster ion beam has incident energy of 3.3 eV/atom. Because the sputter beam with the incident energy above the binding energy in the arginine (about 4 eV [21]) breaks these bonds [12], Ar cluster ion beams with the incident energy of below 4 eV/atom was used for sputtering. The primary ion beam was incident on the solid target at 42° with respect to the surface normal.

In the etching stage of SIMS depth profiling, the target stage raster-scanned the continuous Ar cluster ion beams over an area of 3 mm $\times$ 3 mm. In SIMS analysis, the primary ion beam was chopped twice, with the first and second choppers (chopping width: 2.0 μs and 270 ns, delay time: 55 μs , frequency: 3000 Hz). The choppers were used to select the incident cluster size. In this setup, the size was between 1950 and 2050. The Ar cluster ion beam has incident energy of 5 eV/atom was used in SIMS analysis because protonated arginine molecular ions were measured with high intensity and fragment ions were hardly detected by using the Ar cluster ion beam has incident energy of below 6.7 eV/atom [15]. The size-selected Ar cluster ions were irradiated over an area of typically 0.3 mm $\times$ 0.5 mm to eliminate the edge effect. During 40 s SIMS analysis, up to 1.7×10^{10} ions/ cm^2 were irradiated and the fluence was estimated to be much below the static SIMS limit. Secondary ions were extracted with a kinetic energy of 3 keV and detected with a micro-channel plate (MCP).

3. RESULTS AND DISCUSSION

Figure 2 (a–c) shows the (time-of-flight) ToF-SIMS

spectra of the arginine film before and after 10 keV Ga^+ irradiation at a dose of 1×10^{14} ions/ cm^2 . The intensities of secondary ions were normalized by the values at the peak of m/z 70 ($\text{C}_4\text{H}_8\text{N}^+$). The protonated arginine molecular ion was apparent before irradiation (Fig. 2a), but after Ga^+ ions irradiation, no signal was detected at m/z 175 (Fig. 2b). As the total fluence of 1×10^{14} ions/ cm^2 was far beyond the static limit, the arginine film was seriously damaged with Ga^+ ions. However, characteristic fragment ions, such as m/z 43 ($\text{C}_2\text{H}_5\text{N}^+$, CH_3N_2^+) and m/z 70 were observed with high intensity after Ga^+ ions irradiation. It is well-known that the chemical structure of organic materials is broken and the carbon ratio increases after irradiation with atomic ions [12,22,23], but the material is not carbonized completely at this dose. Figure 2c shows the ToF-SIMS spectrum for irradiated arginine samples at the depth of 30 nm. From Fig. 2c, the ion-induced damage depth was up to 30 nm because the spectrum was almost identical to the one before etching (Fig. 2a).

To convert the fluence into actual depth, a relationship between fluence and sputtering depth must be confirmed. Figure 3 shows the mean sputtering depth for irradiated arginine samples with incident fluence at

Figure 2. Positive secondary ion spectra for arginine films before (a) and after 10 keV Ga^+ irradiation (b,c) at the dose of 1×10^{14} ions/ cm^2 . The depths were 0 nm (b) and 30 nm (c), respectively.

Figure 3. Variation of sputtering depth with Ar_{2000}^+ fluence for the arginine sample irradiated with 10 keV Ga^+ at a dose of 1×10^{14} ions/cm².

10 keV of the Ar cluster ions. The sputtering rates of the bulk and damaged layers were 30 and 23 nm³/ion, respectively. The sputtering rate of the damaged layer was lower than that of the bulk because the former has carbonized and the sputtering rate of carbon is lower than other elements such as oxygen, nitrogen [23]. However, since the damaged layer was only partly, not completely, carbonized, the sputtering rate of the damaged layer was much higher than that of diamond (0.2 nm³/ion).

Figure 4 shows the depth profiles of the characteristic secondary ions for arginine samples. The intensities of secondary ions were normalized by the values at the depth of 70 nm of the profiles, and the incident ion fluence was converted into a depth scale by using the sputtering rates presented in Fig. 3. It was assumed that the bulk and damaged layer could be completely separated from each other because the total fluence of Ga^+ ion was noticeably higher than the static SIMS limit of atomic ions. The positive secondary ion spectrum for irradiated arginine (Fig. 2b) corresponded to that at the depth of 0 nm. As mentioned above, the intensities of the m/z 43 and m/z 70 peaks were very high and that of protonated arginine ion was quite low at the surface. However, these peak intensities decreased rapidly with increasing sputtering depth. In contrast, the peak intensity of the protonated arginine ion increased with increasing the sputtering depth and saturated at the depth

Figure 4. Depth profiles of the characteristic secondary ions for arginine irradiated with 10 keV Ga^+ at a dose of 1×10^{14} ions/cm². The ion beam for both etching and analysis was 10 keV Ar cluster ions.

of about 30 nm. According to the variations in peak intensities (Fig. 4) and spectra (Fig. 2), the ion-induced damage depth was about 30 nm. This value agreed reasonably well with the projection range of 10 keV Ga^+ ion into arginine obtained by TRIM simulation. As mentioned in section 2, it is thought that the effect of sputtering is negligible compared with the damaged layer thickness. This result indicates that the ion-induced damage depth is similar to the projection range of its ion. Ion-induced damage layer thickness on arginine films were accurately evaluated by molecular depth profiling with Ar cluster ion beam.

4. SUMMARY

The damage depth on arginine surface irradiated with 10 keV Ga^+ was evaluated by molecular depth profiling with Ar cluster ion beam. The protonated arginine molecular ion was not detected in the spectrum after etching with Ar monomer beam, indicating that the chemical structure of arginine has been seriously damaged. With increasing sputtering depth the peak intensity of protonated arginine ion grew, saturated at the depth of about 30 nm. This value agreed with the projection range of Ga^+ in arginine. These results indicate that the ion-induced damage depth was the same as the projection range of its ion and accurately evaluated by molecular depth profiling with Ar cluster ion beam.

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